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Pitting Corrosion of 316 Stainless Steel Alloy in Chloride/Thiosulfate Solutions

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ABSTRACT

In this study, the effect of the presence of thiosulfate ion on pitting corrosion of AISI (American iron and steel institute) 316 stainless steel alloy was investigated in four different concentrations of NaCl solutions (1, 0.1, 0.01, 0.001 M NaCl solutions). The experiments were conducted at 50 °C based on the potentiodynamic method. During the experiment, the effect of seven different thiosulfate/chloride concentration ratios were tested (zero, 0.01, 0.03, 0.075, 0.1, 0.2, and 0.3 $S_2O_3^{-2}/Cl^{-1}$ ratios). Pitting potential was recorded for each test. Results show that 316 stainless steel alloy has a passivity region in all tests performed. However, this passivity region was strongly affected by both the chloride concentration and the thiosulfate/chloride concentration ratio. The addition of little amount of thiosulfate to chloride solutions was found to decrease the pitting resistance of the 316 stainless steel alloy. The addition of $S_2O_3^{-2}$ to chloride solutions resulted in a lower pitting potential value at 0.03 thiosulfate/chloride concentration ratio compared to the other ratios.

Keywords
Pitting corrosion.
316 stainless steel.
Thiosulfate ions.

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1 INTRODUCTION

316 stainless steel alloy is one of the most common austenitic stainless steel alloys. Typically, it consists of 18% chromium, 8% nickel, and 2% molybdenum. The presence of chromium, nickel, and molybdenum provides better resistance to localized corrosion such as pitting. For this reason, 316 stainless steel alloy is widely used for sever corrosion conditions such as that in furnaces, heat exchangers, chemical process equipment, and valve and pump parts [1, 2].

Passivity is the state in which the metal corrodes at slower rate, due to the formation of an oxide film on its surface, than it would at some lower potential. This passive oxide film protects the metal surface from dissolving. When the metal surface exposed to environments containing aggressive ions such as chloride and/or thiosulfate, the aggressive ions penetrate the oxide layer at a specific points on the surface, usually at defected points, and increase the rate of metal dissolving:

$$M \longrightarrow M^{n+} + n\,e^- \qquad (1)$$

The electrons produced by this reaction flow from the corroded site (anode) to the nearby metal surface (cathode) where the electrons are consumed by the cathodic reaction. The creation of this local anode site causes a continued build-up of the aggressive ion as well as decrease in the pH which prevents the repassivation of the metal surface. This localized corrosion process is called pitting [2- 4].

Pitting potential is the minimum potential at which localized acidity could be maintained inside the pit. Above this potential, breakdown of passivity occurs, and the rate at which the metal dissolves increases. This cause a continued build-up of aggressive ions inside the pit as well as a decrease in pH. The increase of the aggressive ions concentrations and the decrease in pH prevent repassivation of metal surface. This kind of pit is called the stable pit. Below pitting potential the passive film may break down leading to initiation of pits but these pits repassivate after a short growth. This kind of pit is called unstable pits or metastable pit [1, 2].

The potentiodynamic method is one of the electrochemical techniques used to study the phenomena of pitting corrosion. This technique involves the polarization of the metal electrode at a series of external applied potentials using an electronic device for controlling the electrode potential (potentiostat). Pitting is experimentally determined by monitoring the current density versus the applied potential. The occurrence of the pitting is indicated by a sudden increase in the current density from the passive region (passive current) at a certain potential, known as the pitting potential (Ep) [3, 4].

2 EXPERIMENTAL WORK

In this work, pitting potential measurement was conducted using potentiodynamic technique on 316 stainless steel alloy. The tests were performed using chloride solutions contain zero or little thiosulfate ions at 50 °C. The chemical composition of the material used in this work is given in table 1.

Table 1. The chemical composition of the 316 stainless steel alloy used in this work

Element	Percent
Ni	17.785
Cr	7.859
Mo	2.062
C	0.0345
Mn	1.362
Si	0.475
S	0.002
P	0.018

Al	0.0029
Co	0.0015
Cu	0.007
Ti	0.115
Fe	Balance

The 316 stainless steel specimen was cut from sheet stock with approximately 2.3 cm x 2.3 cm with thickness of 5 mm. The test specimen were mounted in epoxy resin allowing an exposed area of about 4 cm^2 with an electrical connection. The specimen should be mechanically polished before each test. The polishing should be done using emery (silicon carbide) papers ranging from 100 to 1200 grit finish. The specimen then washed with deionized water, and dried with warm air using air dryer. A fresh layer of epoxy patch was applied on the surface of specimen edges (Between the material and the mounting) so that the risk of crevice corrosion is minimized.

The test solutions were prepared from analytical grade sodium chloride (NaCl), sodium thiosulfate ($Na_2S_2O_3$-$5H_2O$) and distilled water. Sodium chloride is the source of chloride ion and sodium thiosulfate is the source of the thiosulfate ion. Four different NaCl solutions were used in these experiments (0.001, 0.01, 0.1, and 1 M NaCl). Solutions of seven different thiosalfate/chloride ratios (Zero, 0.01, 0.03, 0.075, 0.1, 0.2, and 0.3) were prepared for each NaCl concentration.

Potentiodynamic technique were employed in this study. All tests were conducted at 50 °C using a water bath for temperature control and a 500 ml Beaker. The three-electrode system (saturated calomel electrode, platinum auxiliary electrode and test electrode) were immersed directly in the solutions. Applied potential was controlled using the electrochemical cell with a potentiostat type BANK ELEKTRONIC MP 95 and a sweep generator type VOLTAGE SCANNER, WENKING MVS 87. Each test was conducted by anodically polarizing the test specimen at -200 mv (SCE) and then increasing the potential by a rate of 1 mV/sec. Pitting potential was determined by noticing the large rise in the output current. The potential and the anodic current were recorded on a chart recorder type SERVOGOR 102.

3 RESULTS

The corrosion behavior of 316 stainless steel alloy in chloride solutions with and without thiosulfate ions were studied using potentiodynamic method. Typical corrosion behavior of 316 stainless steel alloy in this work is shown in figure 1. This figure represents the behavior of 316 stainless steel alloy in 1 M NaCl solution with zero thiosulfate ion. The figure shows a typical passive region and sudden rise of current at a certain potential, called the pitting potential. The behavior of 316 stainless steel alloy in Cl^{-1} solutions in the presence of thiosulafate ions is the same as shown in figure 1 but at lower pitting potentials. The results show that the occurrence of pitting depends on the chloride ion concentration, addition of thiosulfate ion to chloride solutions and the ratio of thiosulfate to chloride ions.

The effect of chloride ion concentration on pitting potential of 316 stainless steel alloy is displayed in figures 2, 3, and 4. The figures clearly show that increasing the chloride ion concentration shifts the pitting potential to more active values.

The addition of low concentrations of thiosulfate ions to chloride solutions was found to decrease the chloride pitting potential of 316 stainless steel alloy. Figures 2, and 3 show that the addition of $Na_2S_2O_3$-$5H_2O$ to 1 M NaCl solution to form a solution of a ratio of 0.03 thiosulfate/chloride ion, shifts the pitting potential value by 160 mV (from 380 mV to 220 mV). Figures 2, 3, and 4 show that the presence of different thiosulfate ion concentrations shifts the pitting potential of 316 stainless steel alloy to more active values. This shift was found to be depend on the thiosulfate ion to chloride ion ratio. In all different NaCl concentration solutions, the most aggressive $S_2O_3^{-2}/Cl^{-1}$ ratio was found to be 0.03. The pitting potential of 316 stainless steel alloy shows relatively higher values in chloride solutions with $S_2O_3^{-2}/Cl^{-1}$ ratio higher or lower than the critical thiosulfate/chloride ratio of 0.03.

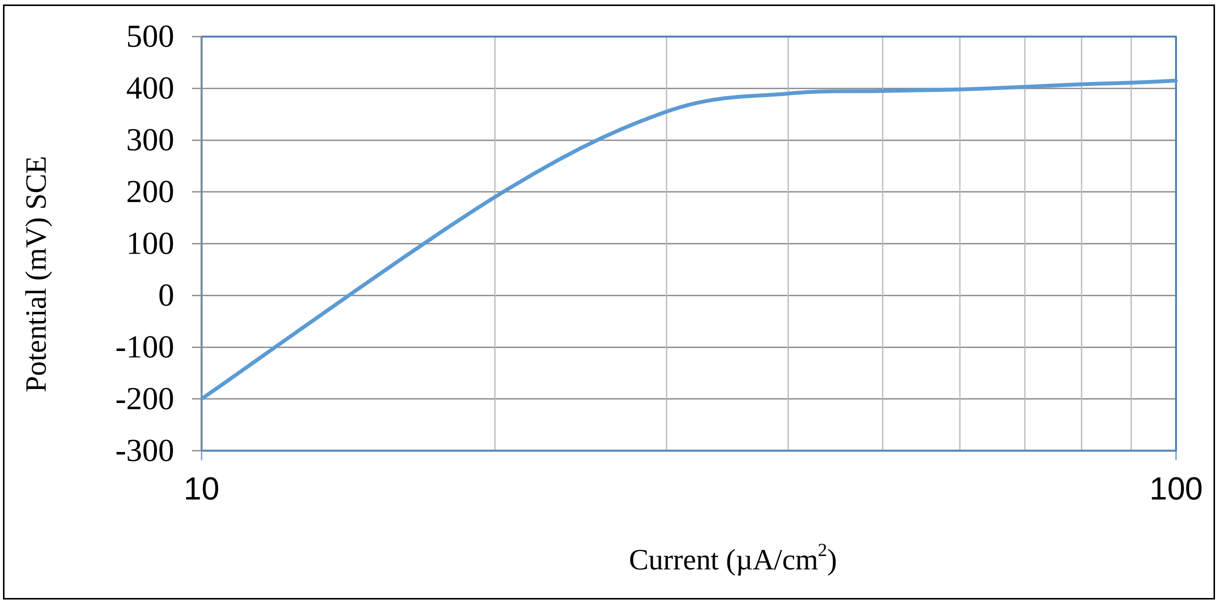

Figure 1. The behavior of 316 stainless steel alloy in 1 M sodium chloride solution (without thiosulfate ions).

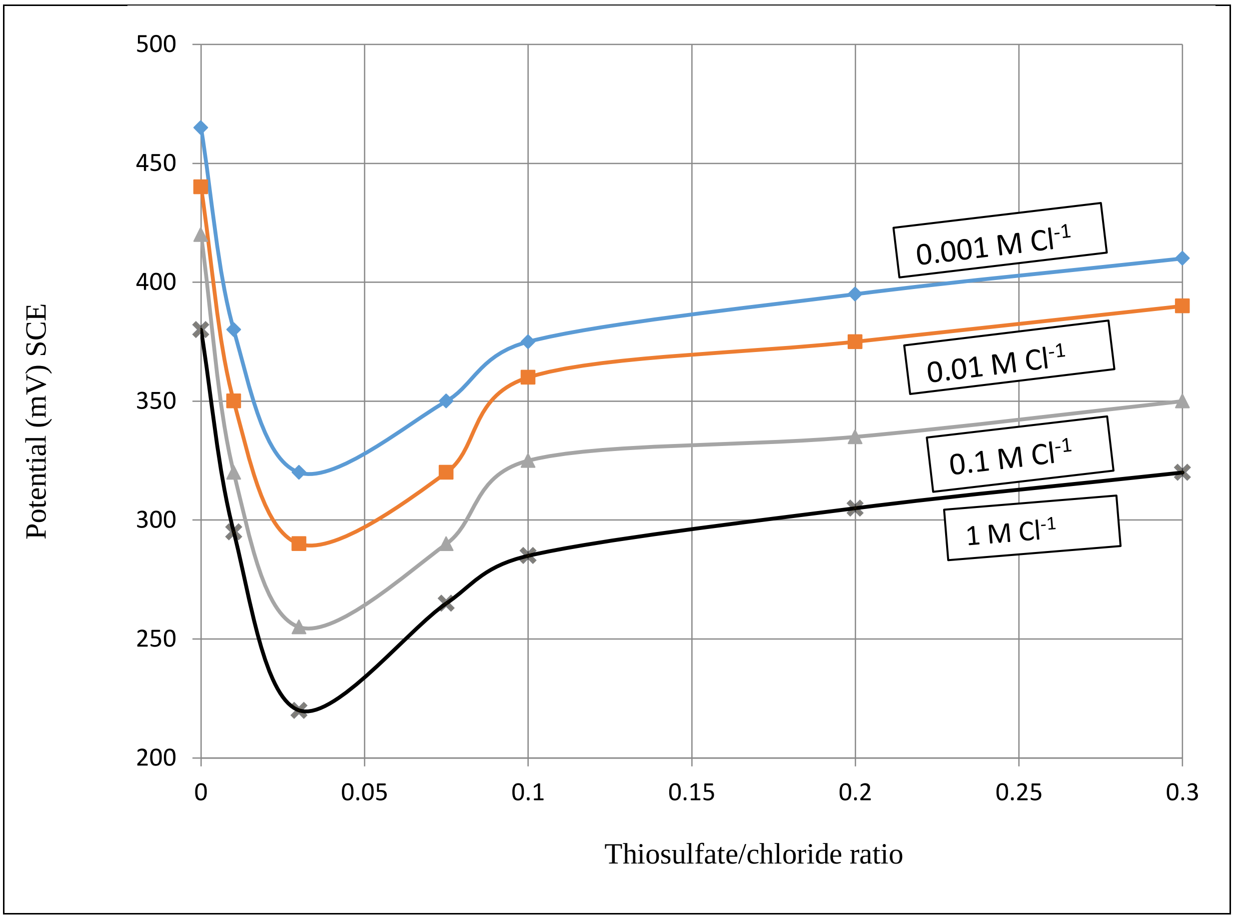

Figure 2. The effect of Chloride ion and thiosulfate ion concentrations on pitting potential of 316 stainless steel alloy.

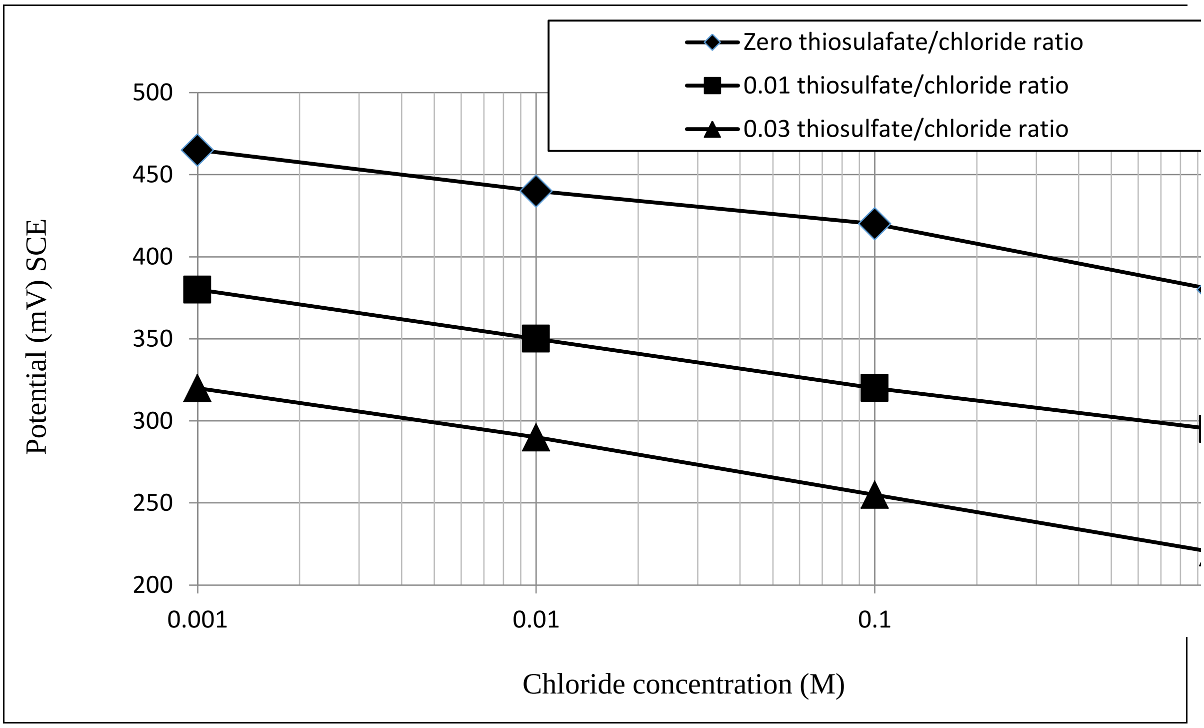

Figure 3. The effect of both the chloride ion and the thiosulfate ion concentrations on pitting potential of 316 stainless steel alloy at zero, 0.01, and 0.03 thiosulfate/chloride ratio.

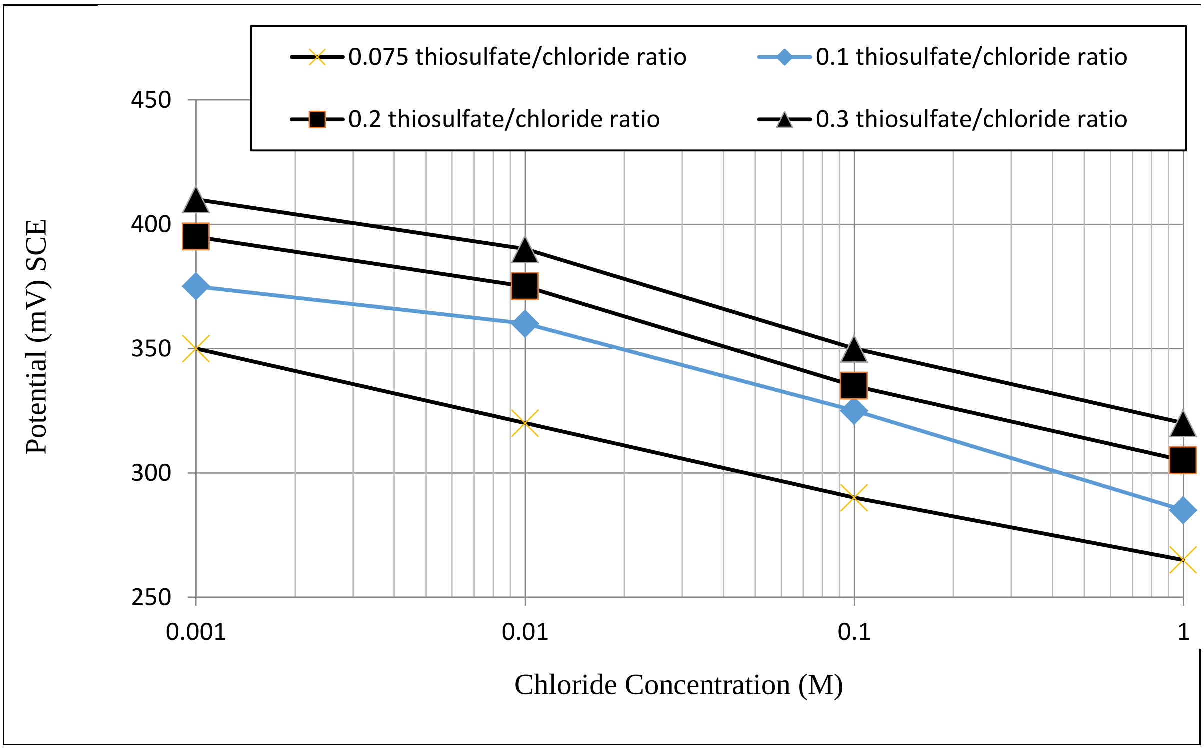

Figure 4. The effect of both the chloride ion and the thiosulfate ion concentrations on pitting potential of 316 stainless steel alloy at 0.075, 0.1, 0.2, and 0.03 thiosulfate/chloride ratio.

4 DISCUSSION

The presence of thiosulfate ion in the test solution leads to the occurrence of the following electrochemical reduction reactions.

$$S_2O_3^{-2} + 6\,H^+ + 4\,e^- \longrightarrow 2\,S_{ads} \qquad (2)$$

$$S + 2\,H^+ + 2\,e^- \longrightarrow H_2S_{aq.} \text{ or } H_2S_{ads} \qquad (3)$$

$$S_2O_3^{-2} + H^+ \longrightarrow SO_3^- + S \qquad (4)$$

The adsorbed sulfur or H_2S activates the anodic dissolution of the metal.

$$(n/2)\,H_2S_{aq.} + M^{+n} \longrightarrow MS_{n/2} + n\,H^+ \qquad (5)$$

The electromigration of Cl^- and $S_2O_3^{-2}$ ions to the pit interior helps the pit to grow. The hydrolysis of Cr^{+3} and other metal ions inside the pit decreases the local pH and provides enough H^+ ions to sustain the thiosulfate reduction reactions as well as to keep the metal surface in an active state.

At values below the pitting potential of chloride ion solutions, unstable pits occur, but after a short time the passive film reformed again and the passivity of the metal regained. If the thiosulfate ion is present in the solution and the unstable pits occur, the thiosulfate ion does not allow the reforming of the passive film by promoting the reduction reactions and then stabilizing the unstable pits.

The rate of electroreduction reactions that produce adsorbed sulfur is effected by the ratio of $S_2O_3^{-2}/Cl^{-1}$. The maximum generation of activated adsorbed sulfur by electrorduction occurred at $S_2O_3^{-2}/Cl^{-1}$ ratio of 0.03. Below and above this ratio, the pitting potential is shifted to higher values. This shift is explained by the slow rate of formation of adsorbed sulfur due to the slow of thiosulfate reduction process at these $S_2O_3^{-2}/Cl^{-1}$ ratios [6].

5 CONCLUSIONS

1- The occurrence of pitting of 316 stainless steel alloy depends on the concentration of the aggressive ions of Cl^{-1} and $S_2O_3^{-2}$. As the concentration of any of the aggressive ions increases the pitting potential decreases.

2- The presence of thiosulfate ion on chloride ion solutions shifted the pitting potential to a lower values.

3- Thiosulfate to chloride ratio of 0.03 is considered to be critical because the pitting corrosion at this ratio occurs at low potentials. If the presence of thisosalfate ion in the chloride ion solutions can not be avoided, the ratio of thiosolfate to chloride ions should be kept away from 0.03 (either greater or less than 0.03).

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التأكل النقري لسبيكة الصلب 316 في محاليل من الكوريد و الثيوكبريتات

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الملخص

في هذا البحث تمت دراسة تأثير وجود أيون الثيوكبريتات على التأكل النقري لسبائك الفولاذ المقاوم للصدأ في تراكيز مختلفة من محاليل كلوريد الصوديوم. كل التجارب أجريت عند 50 درجة مئوية. الطريقة المستخدمة في هذه الدراسة تسمى طريقة الجهد المتغير. تم اختبار نسب مختلفة من ثيوكبريتات /كلوريد (نسب 0 ، 0.01 ، 0.03 ، 0.075 ، 0.1 ، 0.2 ، 0.3)و تم تسجيل جهد التنقر لكل اختبار على هذا الاساس. أظهرت النتائج أن سبائك الفولاذ المقاوم للصدأ 316 لها منطقة سلبية في جميع الاختبارات التي تم إجراؤها. ومع ذلك ، فإن المنطقة السلبية هذه تأثرت على نطاق واسع بكل من تركيز الكلوريد ونسبة الثيوكبريتات/الكلوريد. وجدأن إضافة كمية قليلة من الثيوكبريتات إلى محاليل الكلوريد يقلل من مقاومة التنقر لسبائك الفولاذ المقاوم للصدأ 316. أوضحت النتائج أن إضافة أيونات الثيوكبريتات إلى أيونات الكلوريد بنسبة 0.03 تسبب في تقليل جهد التأكل النقري إلى اذنى مستوى مما ساهم في الاسراع من تأكل سبائك الصلب المقاوم للتأكل.

الكلمات الدالة:
التأكل النقري.
سبيكة صلب 316.
أيون الثيوكبريتات.

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